

DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

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8th Six-Month Report

1 January 1967 - 30 June 1967

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DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

Eighth Six-Month Report
For the Period
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For The
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Grant NsG-458

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INTRODUCTION, ABSTRACT, AND SUMMARY OF EARLIER REPORTS

This report will cover the work performed from 1 January 1967 through 30 June 1967 on Grant NsG-458 between The University of Arizona and the National Aeronautics and Space Administration.

This contract was set up to support the development of new types of detectors for analysis of planetary atmospheres. Initially the interest was in detectors for use under partial vacuum conditions; recently, the program has been extended to include detectors for use at one atmosphere.

Results to date have included detectors for O_2 , H_2 and CO under partial vacuum conditions, (see References Section). More recently, detectors for H_2 and CO in air, at atmospheric pressure, have been reported.

Recently studies have been made on new detectors for oxygen and ammonia. Results indicate that oxygen may be detected at levels near 500 ppm. The ammonia detector has adequate sensitivity at 100 ppm.

Arrangements for commercial production of the carbon monoxide detector have been made. Pre-production designs are being tested and a portable model for field studies is in the planning phase.

RESULTS IN THE LAST SIX MONTHS

Alpha Brass and Ammonia

The study of the reaction between alpha brass and ammonia has progressed and Mr. Anderson has decided to continue this work in the laboratory as a thesis for the M.S. degree.

The alpha brass ammonia reaction is a very characteristic example of stress corrosion. A normally ductile material, alpha brass turns brittle and fractures when exposed to one specific gas, ammonia.

The reaction offers the experimenter an opportunity to study a classical case of stress corrosion with the hope of understanding the basic mechanism. Concurrently it may be possible to use the reaction as a specific detector for ammonia. Ammonia is an important constituent of the atmospheres of the giant planets, where unmanned instrumented probes will almost certainly be used for most investigations. There are other military and life detection applications for an ammonia detector; here, we shall be concerned with the investigation of the fundamental processes of stress corrosion.

The latest experimental set up is shown in Fig. 1. Special grounding rings and an ion shield have been installed; the first to prevent any surface leakage current from the brass wire to the collector, the second to allow the experimenter to remove any ions generated in the air humidifier before they can enter the collector.

For operation controlled and humidified gas mixtures are passed through the system while various voltages are applied between the brass wire and the collector. The positive ion current to the collector is measured by a Hewlett-Packard 425A ammeter and a Heath recorder.

The first experiments with NH_3 and moist air indicated that a small positive ion current to the collector is independent of the presence of alpha brass in the system. We take this current to be due to the normal dissociation of NH_3 in the gas phase; in all later experiments, this small current was taken into account in evaluating the results.

In the next experiments the ion current vs. time curves were observed as a function of NH_3 concentration at constant collector voltage. The results are shown in Fig. 2; in each case, there is a rapid rise in current followed by a plateau, the transition occurring at shorter times with lower concentrations of NH_3 .

To return to the data of Fig. 2, we suggest that the ion current is due to a stress corrosion reaction in which an adherent and protective film forms on the alpha brass and slows down the rate of migration of Zn^{++} ions to the surface and thus to the gas phase.

There is no question that an actual migration of zinc occurs from the brass wire to the positive collector. This is not too surprising because liquid phase SCC is known to involve the loss of zinc from alpha brass leaving behind a spongy, brittle material. Our work is the first to report a similar process in gas phase SCC.

As further proof of this migration, a section of the stainless steel collector was analyzed by x-ray techniques and definite zinc lines were observed. Since the stainless steel showed no evidence of zinc before

We should note that in Fig. 2 and in all subsequent figures the currents have been normalized with respect to I_0 , the current before ammonia is admitted to the test system. This I_0 is somewhat dependent upon the flow rate and moisture content of air flowing through the system. The actual value of $I_0 \sim 10^{-11} - 10^{-12}$ amps is generally constant in a given experiment and dividing the signal by I_0 gives the results in a natural signal-to-noise-ratio form.

the experiment, this may then be taken as definite evidence of zinc ion migration. A subsequent experiment with a conductive glass collector yielded the same results.

Unfortunately, the technique is not quantitative and as yet we have not been able to measure the weight of deposited zinc to compare it with the time integral of the ion current (Faradays experiment). The difficulty involves experimentally weighing the collector to within less than 10^{-6} g which is a rather difficult task without special apparatus and skills.

On the question of zinc migration we feel quite certain that it occurs but not necessarily as Zn^{++} . Zinc forms ion complexes quite easily and in the gas phase the migratory ion might well be $\text{Zn}(\text{NH}_3)_4^{++}$. One of the objectives of Mr. Anderson's M.S. thesis will be the analysis of the ion complex emitted by alpha brass when contacted by moist NH_3 . The JPL mass spectrometer program (discussed elsewhere in this report) will provide a suitable instrument for this experiment.

To return again to the question of the protective film, we note from Fig. 2 that at low NH_3 concentrations the protective film forms very quickly, and the ion current is then constant with time. We suggest that at low NH_3 concentrations the film which forms is relatively defect free and is therefore effective in restricting ionic motion. At higher NH_3 concentrations the film has a greater number of defects and must become much thicker before it begins to limit the flow of ions from the alpha brass to the gas phase.

This explanation of corrosion as a defect controlled migration of ions is the one generally given in corrosion studies⁽¹⁾. In this case

it is in qualitative agreement with our data. As another example, at much higher NH_3/air ratios (not shown in Fig. 2), the film that forms on alpha brass is rough, discolored and non-adherent. The plateau phenomena shown in Fig. 2 is never observed, the ion current increases until the wire is destroyed. This suggests that such films are so defective that they present no effective barrier to ion migration.

To further investigate this defect film theory the next set of experiments involved operating the system at a constant NH_3/air ratio, but with successively larger potentials between the brass wire and the collector. The results are shown in Fig. 3; here we are at an NH_3/air ratio where a protective film normally forms after about 5 minutes of exposure. However, in this case, the higher wire to collector voltages produce an increased slope in the 0-5 min. period and a current which is larger than that observed with a lower accelerating voltage.

Following our earlier suggestion that the corrosion process was controlled by diffusion through the oxide layer on the brass, the data of Fig. 3 may be explained as the effect of the applied voltage on the rate of ionic diffusion in the oxide layer. It is interesting to note that going from 180 volts to 680 volts changes the ion current by less than a factor of 3. This is a typical example of a case where the ion motion is governed more by the defect nature of the film than the applied electric field⁽²⁾.

The increase in ion current from 180 volts to 680 volts was coupled with a change in color and appearance of the oxide layer on the brass. The oxide was definitely darker in current at 680 volts than at the lower voltages. This may be due to ions gaining enough energy from the electric field to create defects or to an actual change in oxide composition with electric field⁽⁴⁾.

Both effects have been observed in anodic oxidation⁽²⁾ and this question is one that we hope to explore in the future. The oxide produced in high electric fields is often somewhat rougher than that produced at zero field and may be less protective against further corrosion. Examples of this are often seen at electric contacts or connections carrying D.C. current, corrosion is much more severe at these points.

The next experiment was designed to determine if the corrosion effect was entirely a surface phenomenon or if the actual bulk structure of the metal was changed by exposure to moist NH_3 . For this purpose a specimen was run at a constant NH_3 /air ratio for some 12 minutes, then removed from the system, cleaned with fine sandpaper, and run again. The results showed quite clearly that the effect is a surface phenomenon with no appreciable change occurring in the bulk metal itself. This is in agreement with the usual theory of alpha brass stress corrosion, at least in the limit of low NH_3 /air concentrations⁽³⁾.

The next experiment was designed to determine if oxygen is a necessary requirement for the observed stress corrosion reaction. We have tacitly assumed this by talking about an "oxide" layer on the brass; however, no data on this point seems to be available⁽³⁾.

For this experiment the moist air, normally used as a diluent for the ammonia, was replaced by ultra pure nitrogen (> 2 ppm O_2). In a 40 minute run, there was no evidence of any ion current or stress corrosion reaction. A similar result was observed with argon, whereas the use of moist oxygen and ammonia led to a very rapid stress corrosion reaction and a large ion current. We conclude that oxygen is indeed required for at least some step in the ammonia-alpha brass reaction.

As a check on the specific nature of the reaction, the ammonia was replaced successively by N_2 , O_2 , CO , CO_2 , A , Freon, and city gas (methane). In no case was any positive ion current observed. This is in agreement with Ref. (1,3) which suggest that alpha brass stress corrosion is specific to ammonia or ammonia compounds.

This concludes our discussion of past experiments; we know that oxygen is necessary for the reaction, that the reaction is proportionate to the NH_3 concentration, that the presence of water vapor speeds up the reaction, and that the rate may be controlled by externally applied electric fields.

We still do not know the mechanism of the reaction, the composition of the oxide film or the exact nature of the zinc-ion complex as it moves from the brass to the collector.

Future Plans

At the moment an experiment is underway to observe the effect of ultraviolet light (UV) on the SCC process. UV might be expected to change the process since other oxidation experiments (Ref. 2) have indicated that oxide layers grown under UV have a relatively defect free structure and are more effective in reducing ion migration than layers grown without UV exposure.

The first experiments seem to indicate that UV light does slow down the brass-ammonia reaction and inhibit stress corrosion. This may have some commercial or military applications but we are not yet ready to report this in detail.

Other planned experiments will include an electron microprobe of the oxide layer to determine its structure and formula. We also plan on an experiment using a mass spectrometer to measure the e/m ratio for the ions

emitted by the brass when exposed to ammonia. This will be part of Mr. Anderson's M.S. thesis.

Application of this reaction between ammonia and brass as a detector for ammonia is a natural outgrowth of this research. Using the higher accelerating voltage data shown in Fig. 3 we can expect to be able to detect as little as 0.01 percent = 100 ppm by volume. This is about the lower limit of human sensitivity (Ref. 5) and obvious applications exist in military areas (for detection of people), in public health (for detection of residual NH_3 in purified sewage intended for reuse, and in planetary and life detection experiments.

The evaluation and ultimate application of our research will be the responsibility of other organizations, and our arrangements for this will be discussed elsewhere in this report. Here we only indicate that while our major effort is in research on surface phenomena, the ultimate justification for the existence of engineering research is the useful results or devices that eventually appear.

Detection of Hydrogen or Carbon Monoxide by Means of the Positive Ion Current from Hot Palladium

In previous reports we have discussed the development of a new type of detector for H_2 and/or CO . A publication reporting this work has appeared (see Publications Section) and arrangements for further developmental work and production have been made with the Burr-Brown Company of Tucson, Arizona.

The Arizona Highway Patrol, the U. S. Public Health Service and several military agencies have expressed interest in the CO detector. Burr-Brown has begun development of a demonstration model of the device and

will solicit contractual support from interested organizations. Professor Hoenig will serve as a consultant on this program but the actual contract management will be done by Burr-Brown.

We feel that this is a valuable arrangement; commercial development is not a university function and Burr-Brown is experienced in this type of work (they manufacture electronic apparatus). This development represents a very practical example of useful "fallout" from the Space Program, with significant Public Health and safety applications.

We expect to continue the investigation of the phenomena itself since the mechanism is still not clear. Part of this investigation has been underway and has already yielded results that are of interest to the semiconductor industry. A short letter to the editor has been written which is reproduced as an Appendix to this report. The letter has been submitted for publication in the Journal of Vacuum Science and Technology.

Chemisorption of Oxygen on ZnO

The studies of chemisorption of O_2 on ZnO have continued and we have been able to obtain some data on the hole trap structure of ZnO layers. This work was done by Mr. M. Lainhart for an undergraduate research project. Mr. Lainhart graduated in June 1967 and Mr. John Lane has taken up the ZnO studies for his M.S. thesis. He will be able to put in more time than Mr. Lainhart and we hope to see the work progress more rapidly.

To quickly review the past results we shall repeat part of the last report.

The test system operates at room temperature and is shown in Fig. 4. The Ultraviolet Source is a mercury discharge lamp manufactured by Ultra-Violet Products, Inc. of San Gabriel, California. Power consumption

is low (7 watts or less with proper design) and efficiency is high since much of the radiation is in the ultraviolet (the band gap of ZnO is about 3.2 eV).

The ZnO is produced by evaporating Zn onto 1" x 3" microscope slides to a thickness of about 5000 Å. The slides are oxidized at 500°C in oxygen for seven or eight hours. Electrical contact is made by means of platinum strips pre-fired on the slide or with silver paint. This ZnO-on-glass system is quite stable, some specimens have been in use for four months with no detectable change in characteristics.

Operation is straightforward, the ultraviolet source is left on at all times and the gas flow to the system is cycled from a standard, i.e., pure (bottled) N₂, to the O₂/N₂ mixture under investigation. The conductivity of the specimen is monitored by means of a voltage source (1.4 V dry cell) and a Hewlett-Packard 425 A microammeter. Typical currents are about 150 microamps; the output of the microammeter is recorded on a Heath Co. EUW-20 recorder.

Before presenting the data we must quickly review the pertinent properties of ZnO. In the dark and in the absence of oxygen ZnO is an n type semiconductor with no band bending at the surface. If oxygen is admitted to the system, a rapid drop in ZnO electrical conductivity occurs. This is due to the formulation of O₂⁻ and/or O⁻ ions on the surface of the ZnO. The oxygen comes from the gas phase, the electrons from the conduction band of the ZnO. This loss of electrons is partially responsible for the rapid drop in electrical conductivity when oxygen is adsorbed by ZnO. The remainder of the drop in conductivity is due to the forcing of free electrons away from the vicinity of the surface by the immobile layer of O₂⁻ and O⁻.

This latter effect is especially important when the ZnO is in the form of a thin film since the effect of the immobile surface layer extends entirely through the film. This effect on the band structure of the ZnO is shown in Fig. 5 (taken from Ref. 6). The formation of the ionized O_2^- , O^- layer is shown by the upward bending of the bands near the surface.*

In any event the decrease in current continues at a decreasing rate as long as there is oxygen present. "Fast" and "slow" states may be distinguished and this will be discussed in more detail later.

If at some moment the ambient oxygen is pumped away and the ultra-violet light is activated, the oxygen adsorption process is reversed and the electrical conductivity of the ZnO begins to increase. This desorption process is dependent upon creation of electrons and holes by the incident ultra-violet light. The electrons have relatively little effect since the ZnO is already n type but the holes are drawn to the surface by the negative surface layer (due to O_2^- and O^-). Upon arrival at the surface they acquire electrons from the adsorbed O_2^- and O^- ions. The oxygen is desorbed as O_2 and may be pumped away.

Given this introduction we can discuss the results of what we shall refer to as Mode I operation. Mode I is intended for rapid detection of oxygen at partial oxygen ratios $V_{O_2}/(V_{O_2} + V_{N_2})$ from 1 to 10^{-4} . In Mode I the ultraviolet source is kept on at all times during operation. Warm up and calibration is accomplished by direction of a small flow of gas of known oxygen concentration, (i.e., tank nitrogen) to the detector for a five minute period. At the end of this time a controlled flow of O_2 is mixed with the N_2

* We should mention that Collins and Thomas⁽⁷⁾ have questioned this conventional interpretation but to date their suggestion has received little support.

flow to the detector. The drop in current is monitored for 60 sec. and then the oxygen flow is turned off while the calibration gas, (N_2) continues to flow through the system. The detector recovers to its base line in about 75 seconds and is then ready for use again.

The detector output is quite repeatable not only from run to run but from week to week. As evidence of this we show Fig. 6. Figure 6 gives the result of twelve runs made over a period of days. Each run was made at the same volumetric flow ratio $V_{O_2}/(V_{O_2} + V_{N_2}) = 0.5$ but with different values of V_{N_2} , V_{O_2} . It is clear that the response of the device is quite repeatable in the detection and recovery parts of the run.

In Fig. 7 we show the response of the detector at various values of the parameter $\alpha = V_{O_2}/(V_{O_2} + V_{N_2})$ versus the current ratio after the oxygen is admitted to the system. It is clear that the final current value is directly related to the partial volume of oxygen.

This is best seen in Fig. 8 where we have plotted the current ratio after 60 seconds of exposure to a given O_2/N_2 mixture.

$$(I/I_0)_{60} \text{ vs } \alpha = V_{O_2}/(V_{O_2} + V_{N_2})$$

The log, linear plot is effectively a straight line over three orders of magnitude.

We have added to Fig. 8 some of the new data generated during the last six months. These results represent part of our effort to improve the system as a potential detector for oxygen while at the same time gaining more understanding of the physics of the chemisorption process.

These new results extend the sensitivity of the ZnO - oxygen system to an α of $5 \cdot 10^{-4} = 500$ ppm. This higher sensitivity is an effect of

I_0 , the current before oxygen is admitted. To see this we compare curve A in Fig. 8 with curve B where I_0 was 100 times larger. At low values of α (i.e., $9 \cdot 10^{-3}$) the signal to noise ratio for curve A is 1.4 while that of B is only 1.02. Clearly at low values of α slide A would be much more satisfactory than slide B.

Conversely, we would expect that at high values of α slide A would saturate and therefore give no useful output. Slide B would be more useful in this high α range.

This is an example of how the operational characteristics of the system can be modified by careful control of slide thickness, grain size and composition. The slide which yielded curve B was made in the usual manner by evaporation of zinc and slow oxidation at 500°C . This yields a zinc rich material with tightly packed grains and a high conductivity (high I_0).

The slide which yielded curve A was made by exposing a pyrex slide to the fumes of zinc burning in an oxygen rich hydrogen-oxygen flame. The grain size is coarser, and the ZnO is probably close to the stoichiometric composition. This results in a low conductivity and a high sensitivity because the oxygen can easily enter the coarse structure of the ZnO .

One of our most important objectives is the development of controlled fabrication techniques for ZnO . At present, the evaporation and oxidation process is not capable of yielding samples of predictable grain size and thickness.

We know that the rate of evaporation of Zn and the rate of oxidation to ZnO are important and one of Mr. Lane's objectives will be measurement of these parameters.

There are reasons for believing that the density of hole traps in ZnO is an important parameter in the response of ZnO to light⁽³⁾. Our first

experiments on this question will be discussed below; we feel that there is a direct connection between the thickness and grain size of the ZnO and the hole trap density. It should be mentioned that measurement of ZnO thickness and grain structure has been a severe problem because most optical interference techniques require a highly reflecting surface. Staining might be possible but this would change the slide composition and characteristics. To date best results have been achieved with a new material called Press-O-Film, manufactured by Testex, Inc. of Newark, Delaware 19711. For use the ZnO is produced with a step equal to the ZnO thickness. The soft and reflective Press-O-Film is then pressed against the ZnO to allow it to replicate the step contour. After replication, the film is stripped off and examined by standard interference microscope techniques.

Results with this technique are reasonably satisfactory but we are still learning how to handle the Press-O-Film. If one presses too hard, the ZnO and the Press-O-Film are ruined.

Optical and Thermal Phenomena in ZnO

Studies of the optical response of ZnO are an obvious part of the use of ultraviolet light to recycle ZnO. In our earlier reports we discussed the use of thermal cycling and at this point we consider both phenomena.

Considering that ZnO is an oxygen poor extrinsic semiconductor, we can appreciate that it is not possible to directly calculate the expected response of the conductivity to temperature. However, the work of Heiland⁽⁹⁾, pg. 253, indicates that his samples were extrinsic and thermally induced conductivity changes were small between 300°K and 700°K.

Our earlier tests indicated that for a temperature range of 300°K to 600°K the conductivity change was less than a factor of 7. If our samples

were intrinsic, the change would have been over 1000 and we conclude that our samples are extrinsic and thermally generated charge carriers will have little effect on the measured currents. This may be clarified by considering that if the ZnO is a strongly extrinsic n type material, any thermally generated holes will quickly recombine and holes will not contribute to the measured conductivity. The thermally generated electrons will make only a small addition to the large number of extrinsic electrons and in the limit of low electron mobility the effect of the thermal electrons will be relatively small.

Turning now to the optical data we see in Fig. 9 the change in current with time when ZnO is exposed to UV in pure N_2 . The upper curve shows the usual fast and then slow rise normally observed. Recalling that the band gap of ZnO is 3.2 ev and that the UV source has a quartz envelope, it is clear that there is ample radiation for excitation and trap emptying.

In this connection we might note that photons of energy 1 ev have a wavelength of 12500\AA . We can expect that even the blue end of the visible spectrum (4000\AA) will have enough energy to excite electrons across the band gap.

This can be contrasted with thermal photons which at 300°K have an average energy of about 0.026 ev. It is easy to see why light has more effect on ZnO than heat.

Returning to Fig. 9 the lower curve was obtained with a No. 8 wratten filter between the UV source and the ZnO. The filter cuts off all radiation below 4500\AA and the lower curve shows a long slow rise which we take to be the emptying of hole and electron traps because 4500\AA Photons do not have sufficient energy to excite electrons across the 3.2 ev band gap.

At this point we have given strong evidence of the presence of hole and electron traps but no information as to the relative numbers has been obtained. If, however, we recall our earlier discussion of the adsorption-desorption process of O_2 on ZnO, we can suggest that O_2 be used as a probe to measure the hole concentration in the ZnO.

If O_2 is admitted to the system the effect on the measured ZnO conductivity is a balance between the adsorption of O_2 to O_2^- and the desorption of O_2^- because of neutralization by holes.

Using this concept the density of holes at any time may be measured by introducing a known quantity of oxygen and noting the effect. The more effect on ZnO conductivity the fewer holes and vice versa. The result of such an experiment is shown in Fig. 10. (Fig. 10 is a composite of several runs and the numerical values are not strictly comparable to Fig. 9).

To obtain the data of Fig. 10, the UV light was activated and at some time near equilibrium (7 min.) a fixed quantity of oxygen was admitted. If we take the ratio

$$\frac{I_{7 \text{ MIN.}} - I_{10 \text{ MIN.}}}{I_{7 \text{ MIN.}}} = 1/\beta$$

as a measure of the effect of the O_2 on the ZnO, it is clear that the oxygen had more effect on the lower curve $\beta = 1.54$ than on the upper $\beta = 1.22$. This indicates that relatively few holes exist at this late (7 min.) time since most hole traps have been emptied and the holes lost by recombination.

With no filter, holes are created continuously by radiation of $\lambda < 4000\text{\AA}$. With the filter in place, this is not possible and the oxygen is more effective in terms of lowering the ZnO conductivity.

The situation is different during the fast rise of current just after the UV is turned on. In Fig. 11 we show the current time curves with and without the wratten #8 filter and with and without oxygen admitted at 0.5 min. Now the oxygen has essentially no effect indicating that at 0.5 min. there are ample holes to desorb the O_2 as fast as it adsorbs. This is true even with the filter in place which indicates that the holes are primarily from traps.

We feel that this study has demonstrated the existence of hole traps in ZnO and their importance in the early "fast" rise in ZnO conductivity.

Future Plans

We hope to continue the study of ZnO with the hope of learning more about the physics of chemisorption. The next experiments will cover the effects of electric fields and other gases on ZnO conductivity.

Other Activities in the Laboratory Related to this Program

A study of stress corrosion of uranium - 10% molybdenum has been underway for the past 10 months. The program is supported by the U. S. Army Aberdeen Proving Ground as Contract #DA-18-001-ANC-1063(x). U-10% Mo is stress corroded by oxygen and much of our experience with alpha brass has been applicable to U-10% Mo.

Results to date indicate that dislocation motion under applied stress is the major factor in stress corrosion cracking of U-10% Mo by oxygen. Some progress in improving the SCC resistance of U-10% Mo has been made. We are now in the stage of extending the experiments on controlled surface deformation to larger specimens.

A contract (JPL No. 951560) for development of a field ionization source for a mass spectrometer has been received from JPL. This contract

is directly related to the objective of NSG-458 especially since the recent work of Beckey indicates that different isomers of hydrocarbon compounds (i.e., 1 vs 2 hexene, C_6H_{12}) of equal molecular weight (and e/m ratio) may be separated by their behavior in a field ionization system.

The JPL contract has added some important and expensive pieces of apparatus to the laboratory stock and has brought us into close connection with a major NASA contractor. The field ion source has been operating with the Ultek quadrupole mass spectrometer and one of the first spectrums is shown in Fig. 12. The gas was $N_2 + A$ and the resolution leaves much room for improvement, but to the best of our knowledge this is the first such spectrum obtained with field ionized ions and a quadrupole mass spectrometer.

We have in the past discussed cooperative work with the University Lunar and Planetary Laboratory. This work is continuing, the studies of ion bombardment of simulated lunar soils have been finished and a report is in preparation by LPL personnel. Studies of the melting of volcanic rocks under vacuum conditions are still underway. Evidence has indicated that these vacuum melted rocks are similar in many ways to the surface structure of the moon.

We are cooperating with Dr. Aden B. Meinel, Director of the University Optical Studies Program, on experiments to develop improved astronomical optical detectors. This is a natural adjunct to the other surface studies underway since certain optical detectors (phototubes) are dependent upon surface phenomena.

Mr. Greg Smith joined us in September, 1966, as a Ph.D. candidate in Electrical Engineering. He has begun studies of photoelectric surfaces with a view toward increasing the sensitivity and lowering the energy

threshold for emission. Support from the Astronomy Department and the University NASA Grant has allowed this program to proceed without problems. A capability in optical techniques will give us another method for investigation of surface properties of materials.

Some results of this program have appeared and are listed⁽⁹⁾ in the Publications Section.

PUBLICATIONS GENERATED TO DATE BY RESEARCH ON CONTRACT NSG-458

(S. A. Hoenig and others)

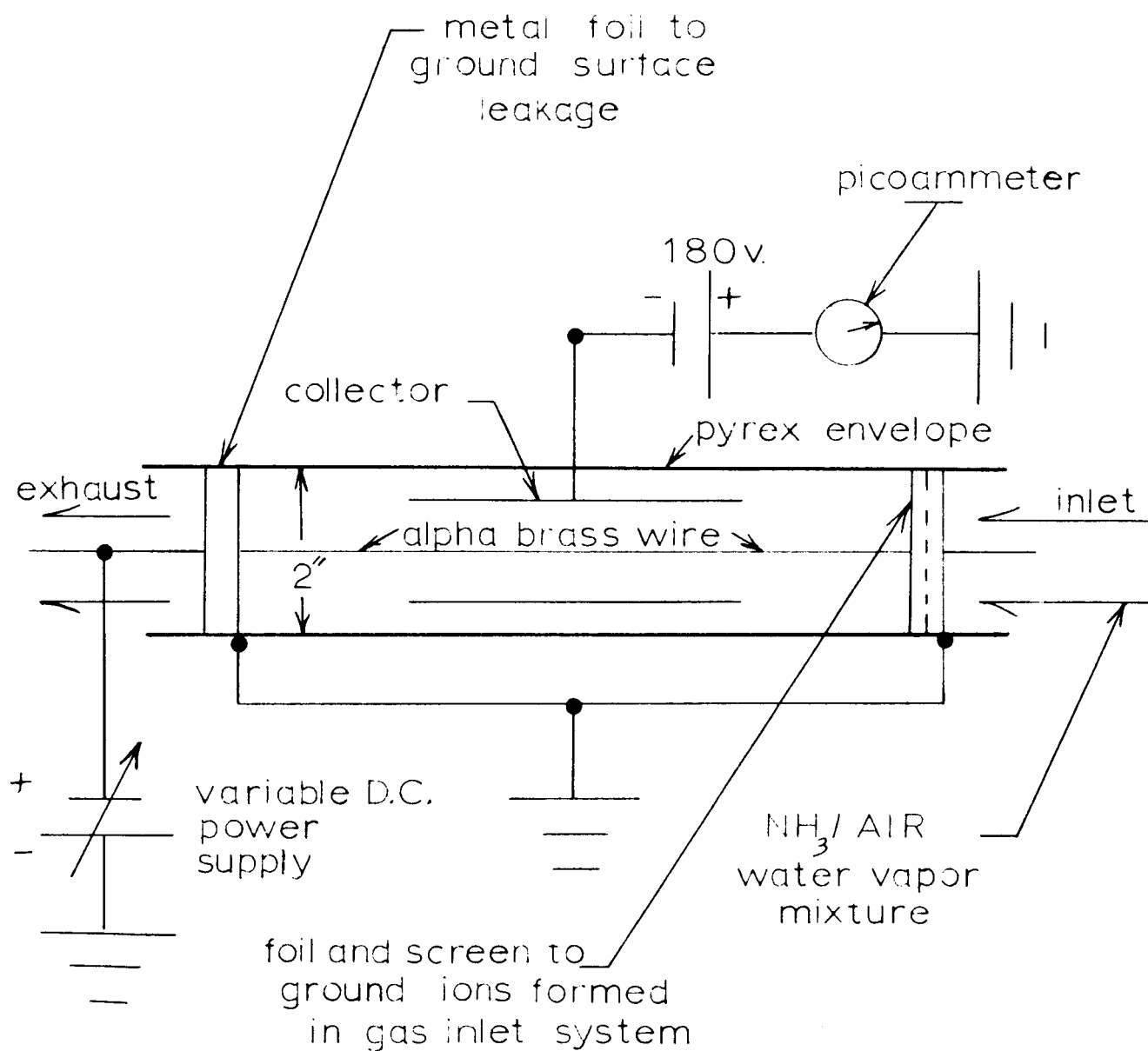
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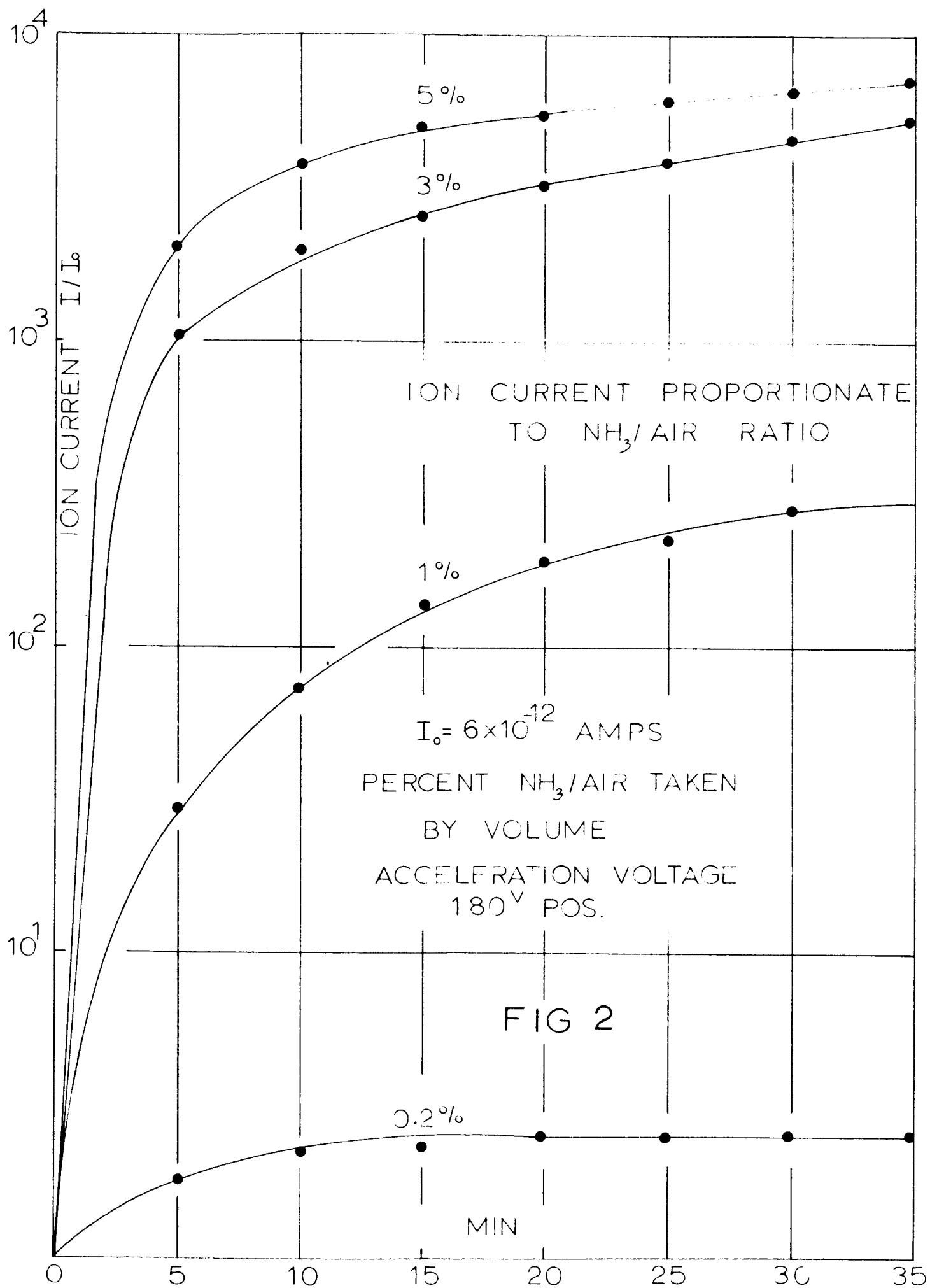
FIGURES

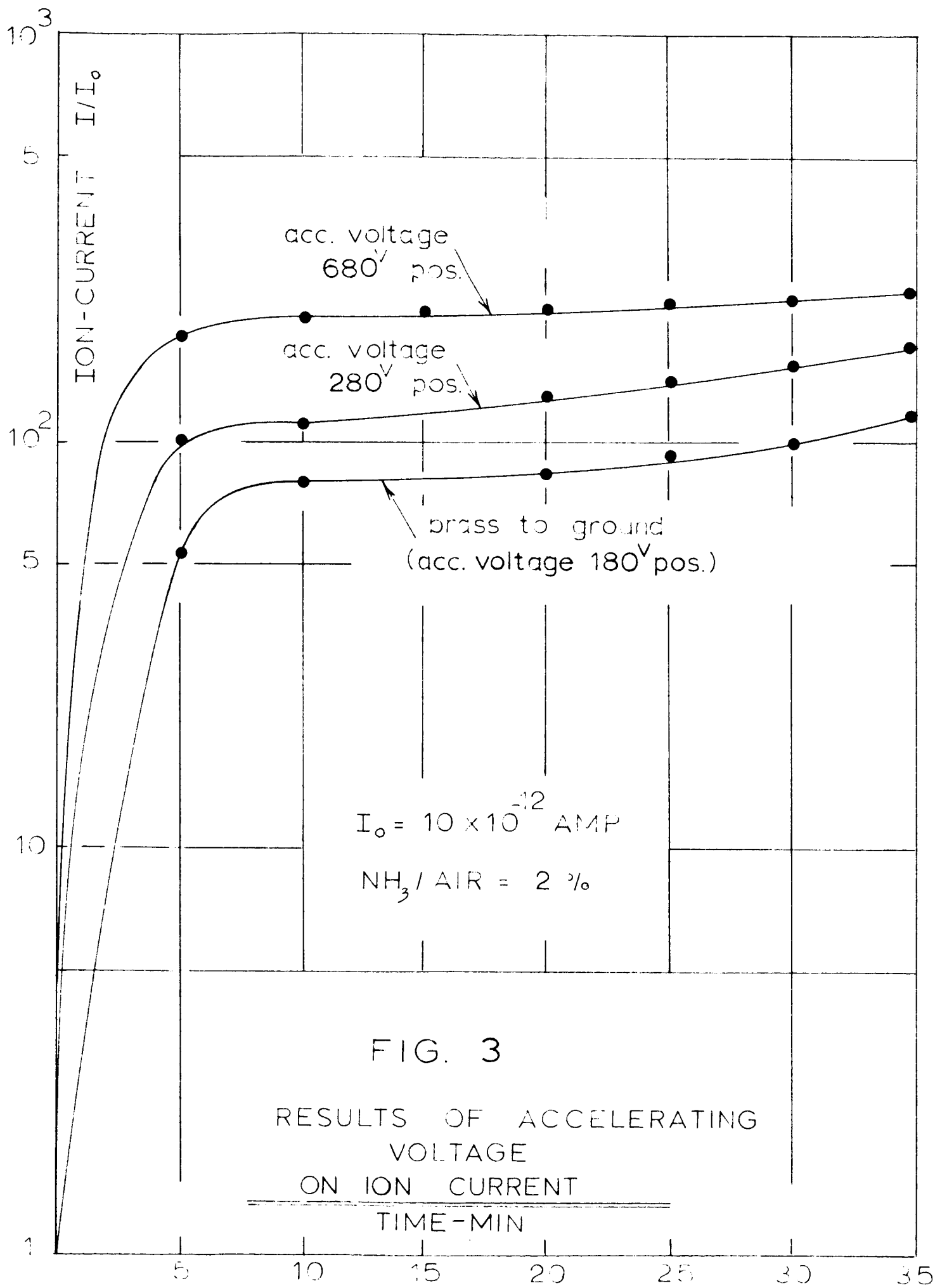
1. Alpha Brass Ammonia Stress Corrosion Apparatus
2. Effect of NH_3 /air Ratio on Positive Ion Current
3. Results of Accelerating Voltage on Ion Current
4. ZnO - O_2 Detector System
5. ZnO Band Structure
6. Response of ZnO to O_2 While UV Source Activated
7. Response of ZnO Detector System
8. ZnO - O_2 Detector Calibration Curve
9. ZnO Current vs. Time in Pure N_2
10. ZnO Current vs. Time
11. ZnO Current vs. Time
12. Field Ion Spectrum of N_2 , a Mixture



ALPHA BRASS AMMONIA STRESS
CORROSION APPARATUS

FIG. 1





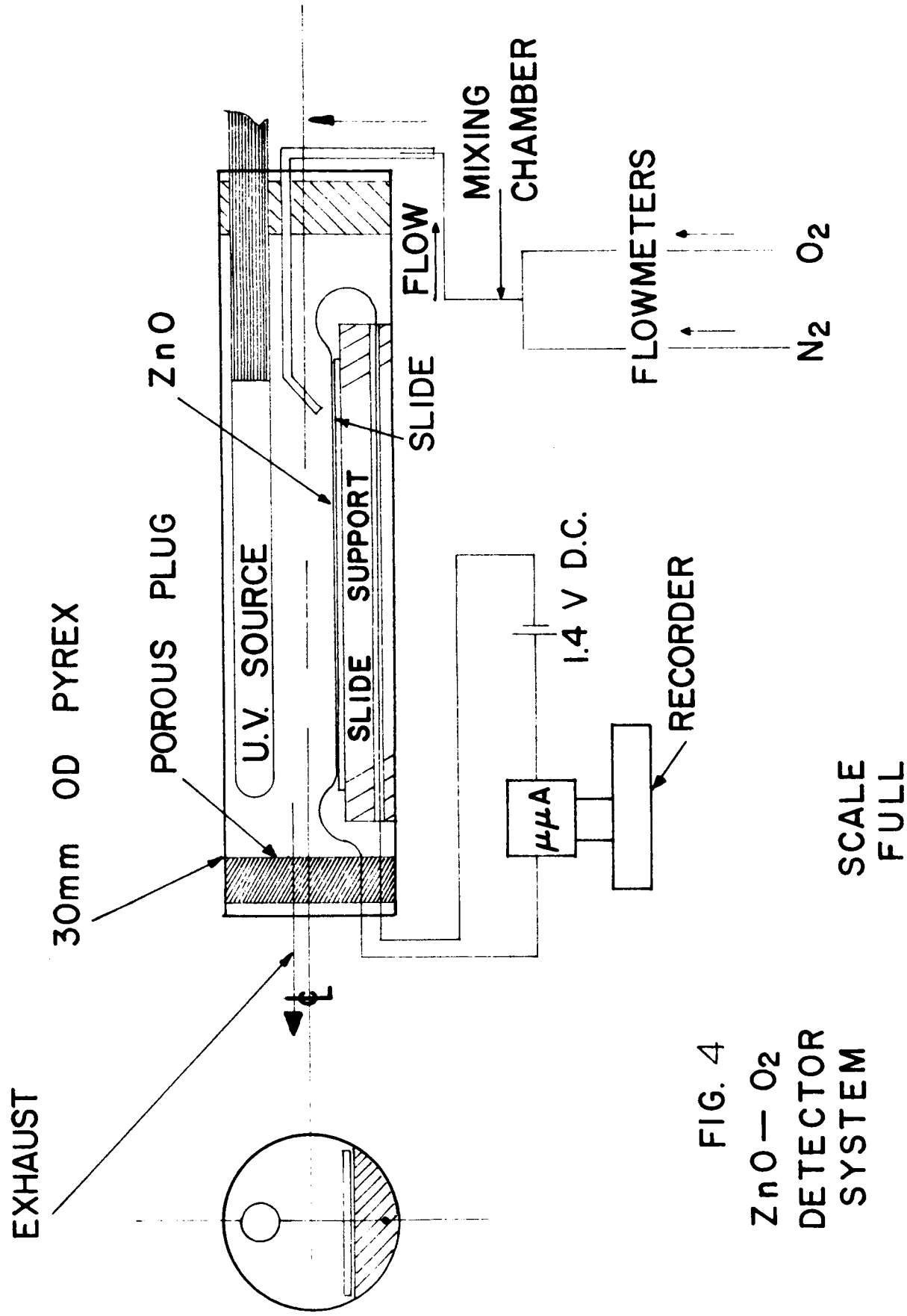
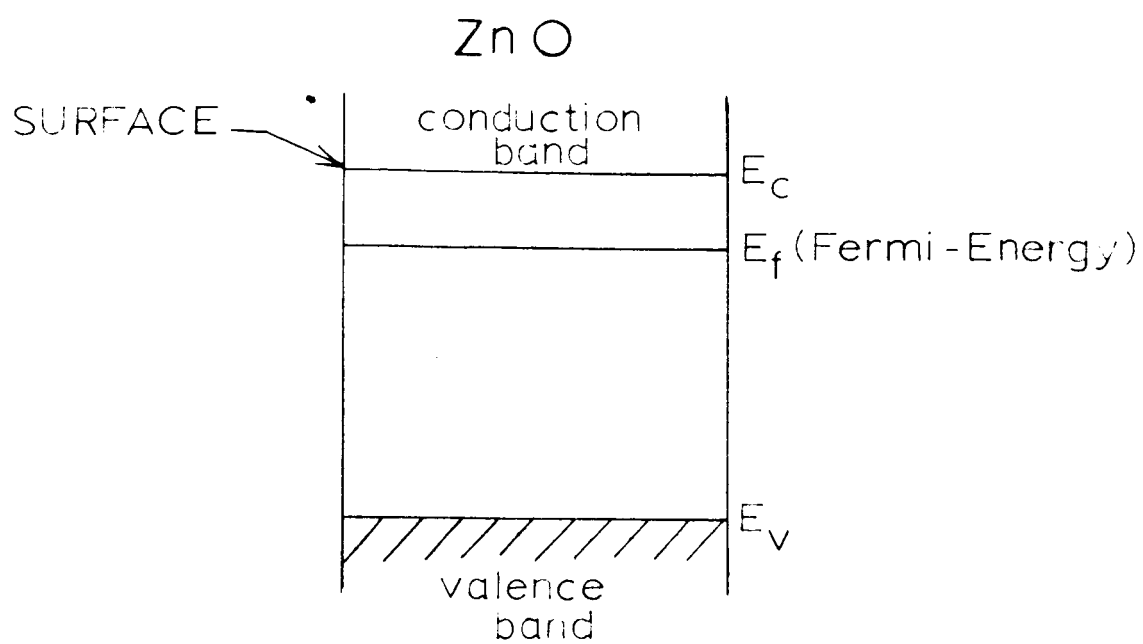
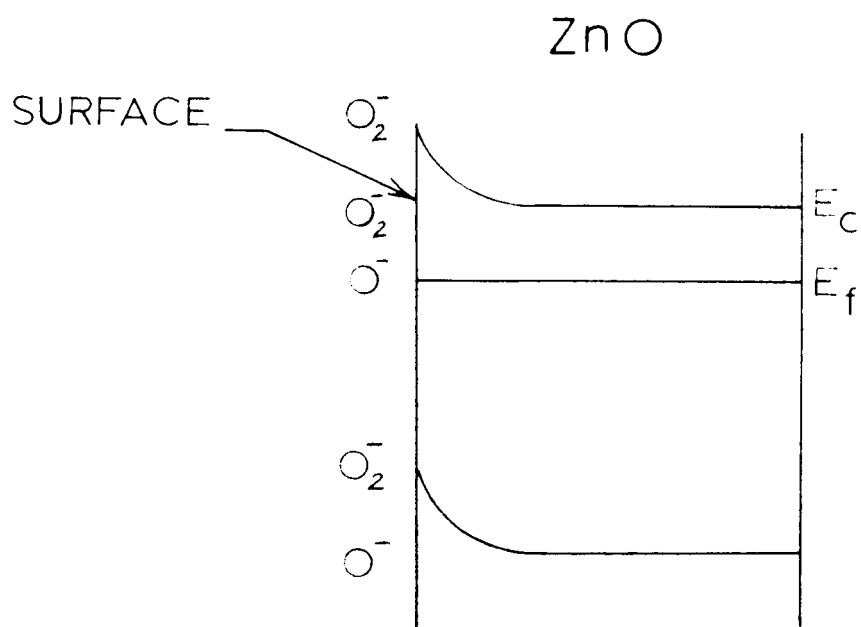


FIG. 4
ZnO — O₂
DETECTOR
SYSTEM



ZnO IN DARK, GAS FREE, ENVIRONMENT

FIG. 5a



ZnO AFTER EXPOSURE TO OXYGEN

FIG. 5b

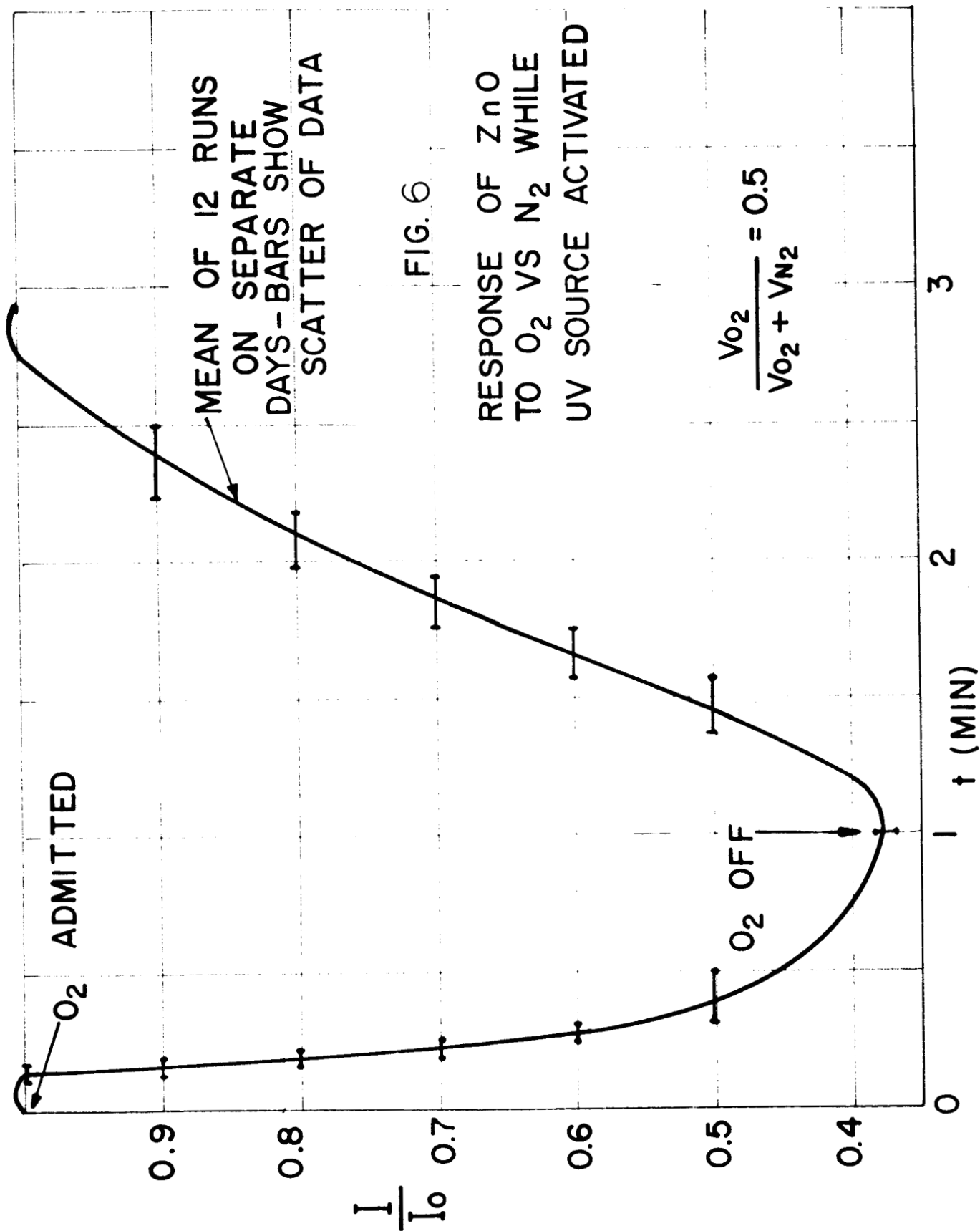
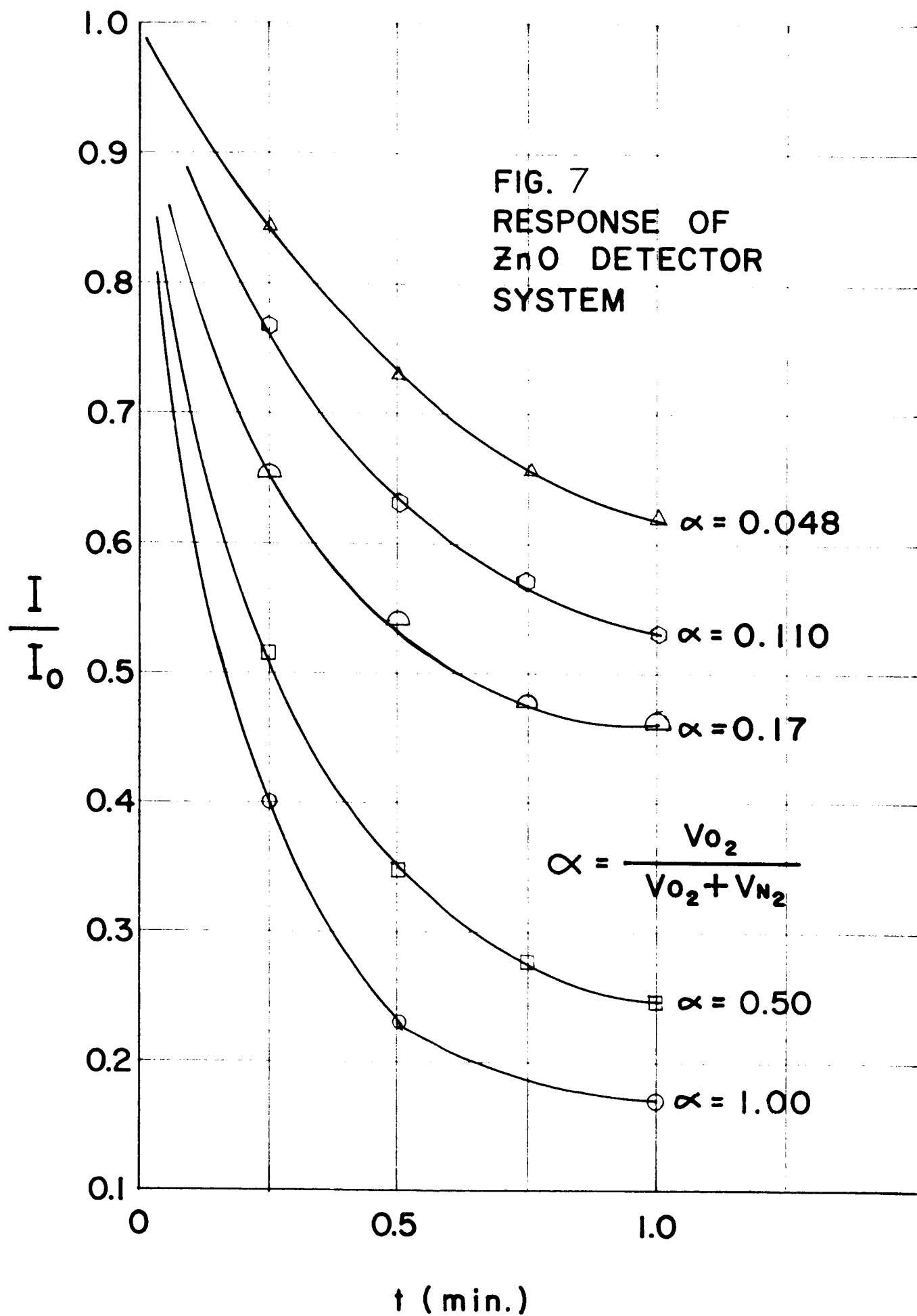
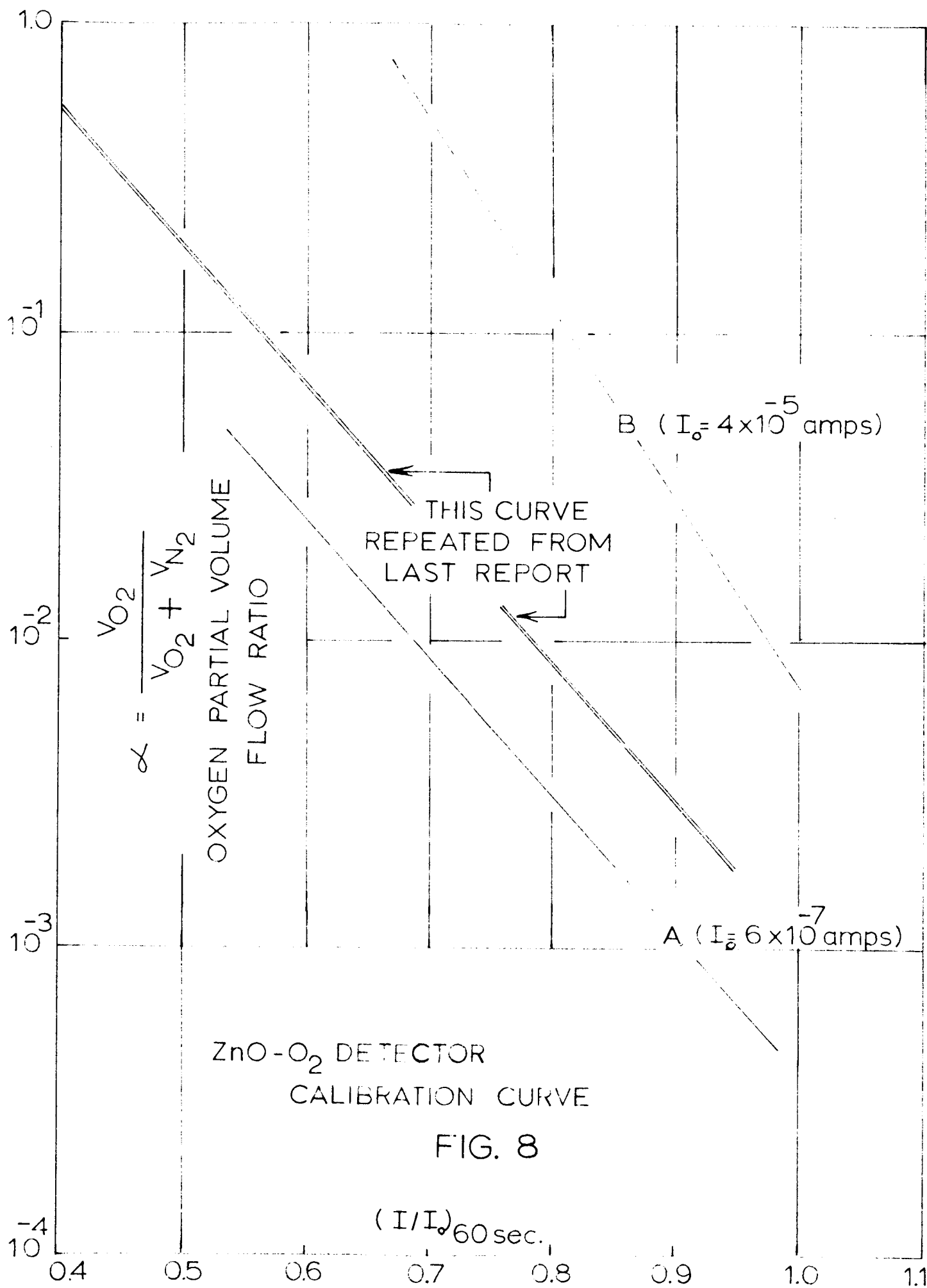


FIG. 7
RESPONSE OF
ZnO DETECTOR
SYSTEM





FILTER = #8 WRATTEN (4600 Å CUT OFF)

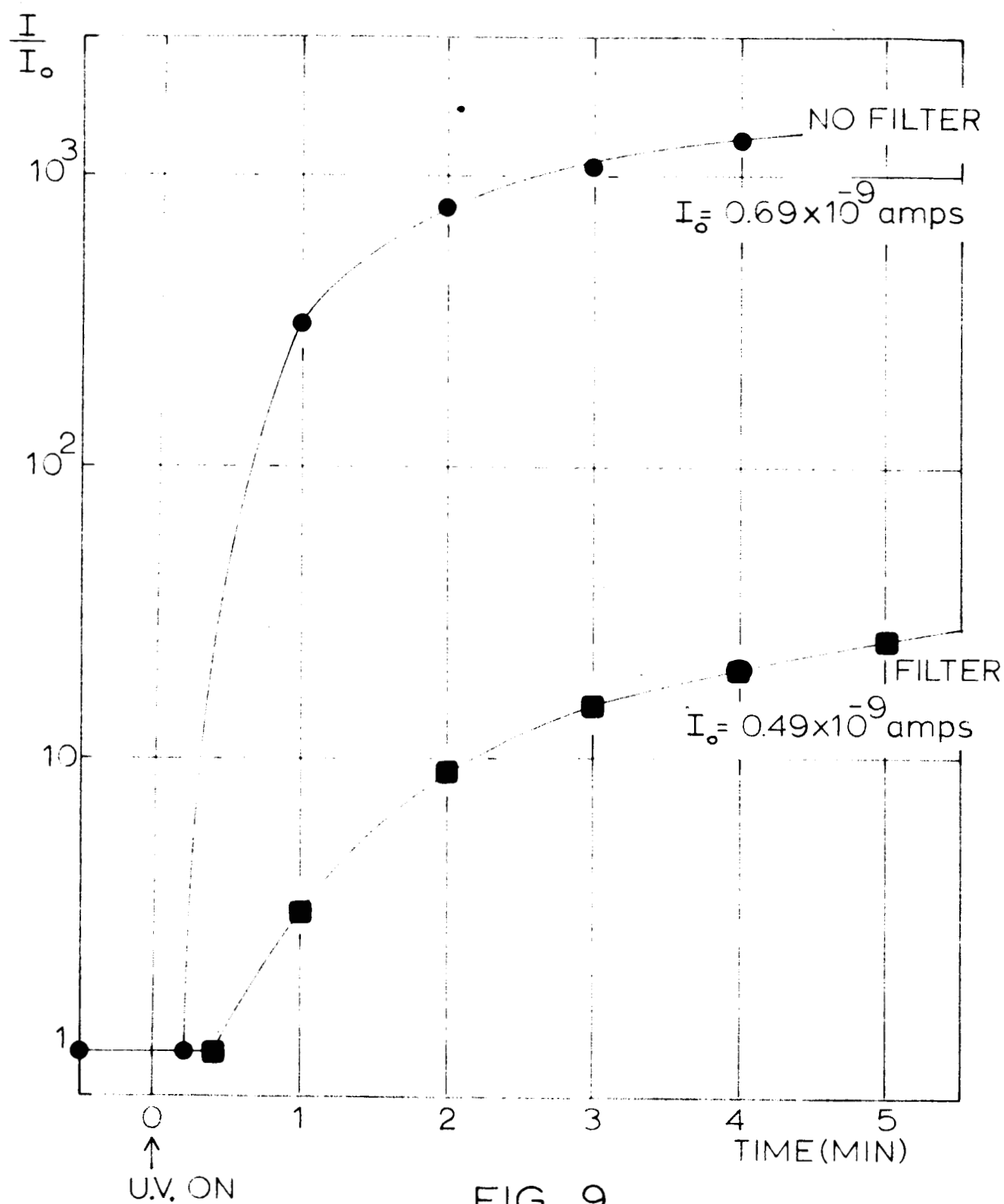


FIG. 9

ZnO CURRENT vs TIME IN PURE NITROGEN

FILTER = #8 WRATTEN (4500Å CUT OFF)

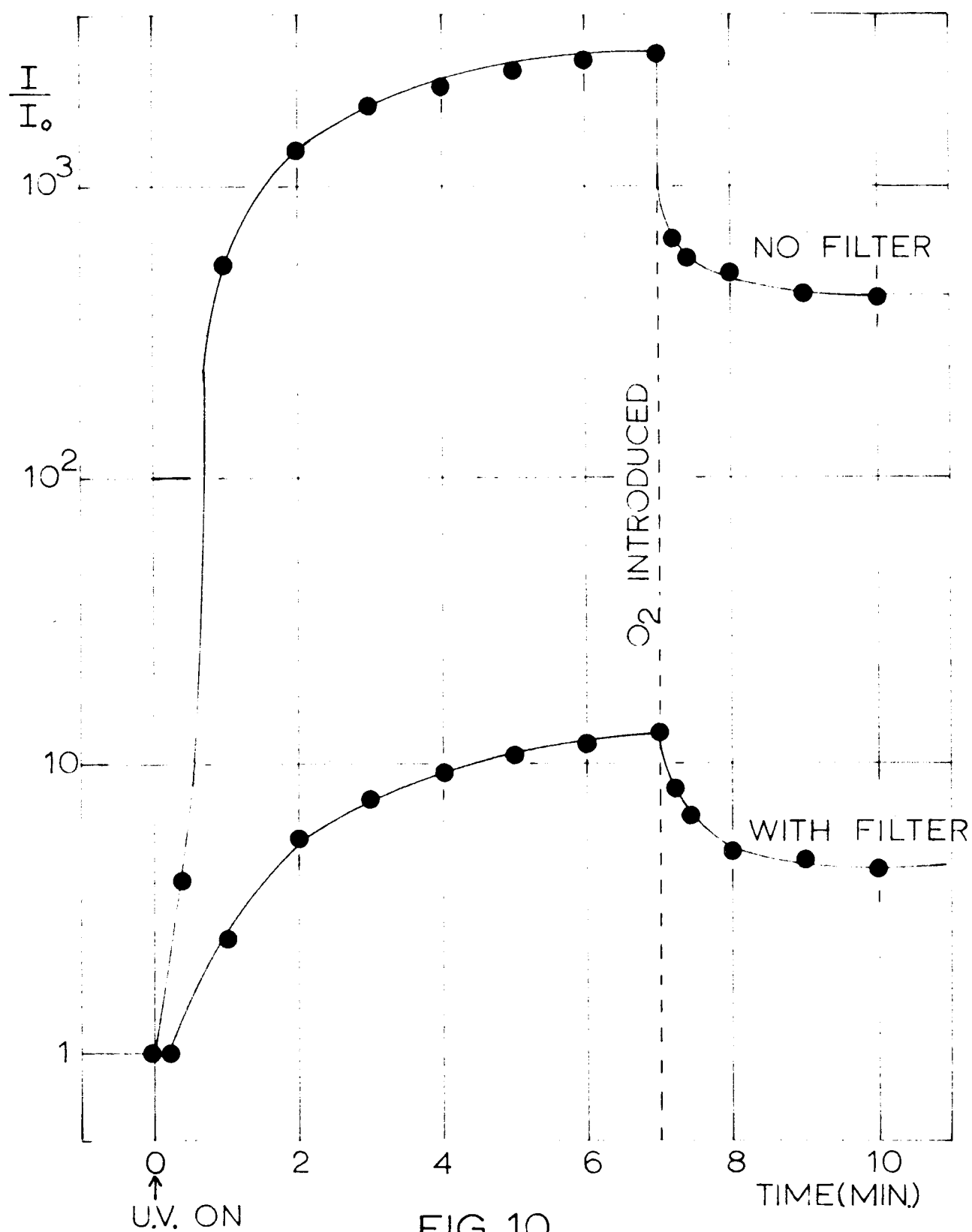


FIG. 10

ZnO CURRENT vs TIME

FILTER = #8 WRATTEN (4000 Å CUT OFF)

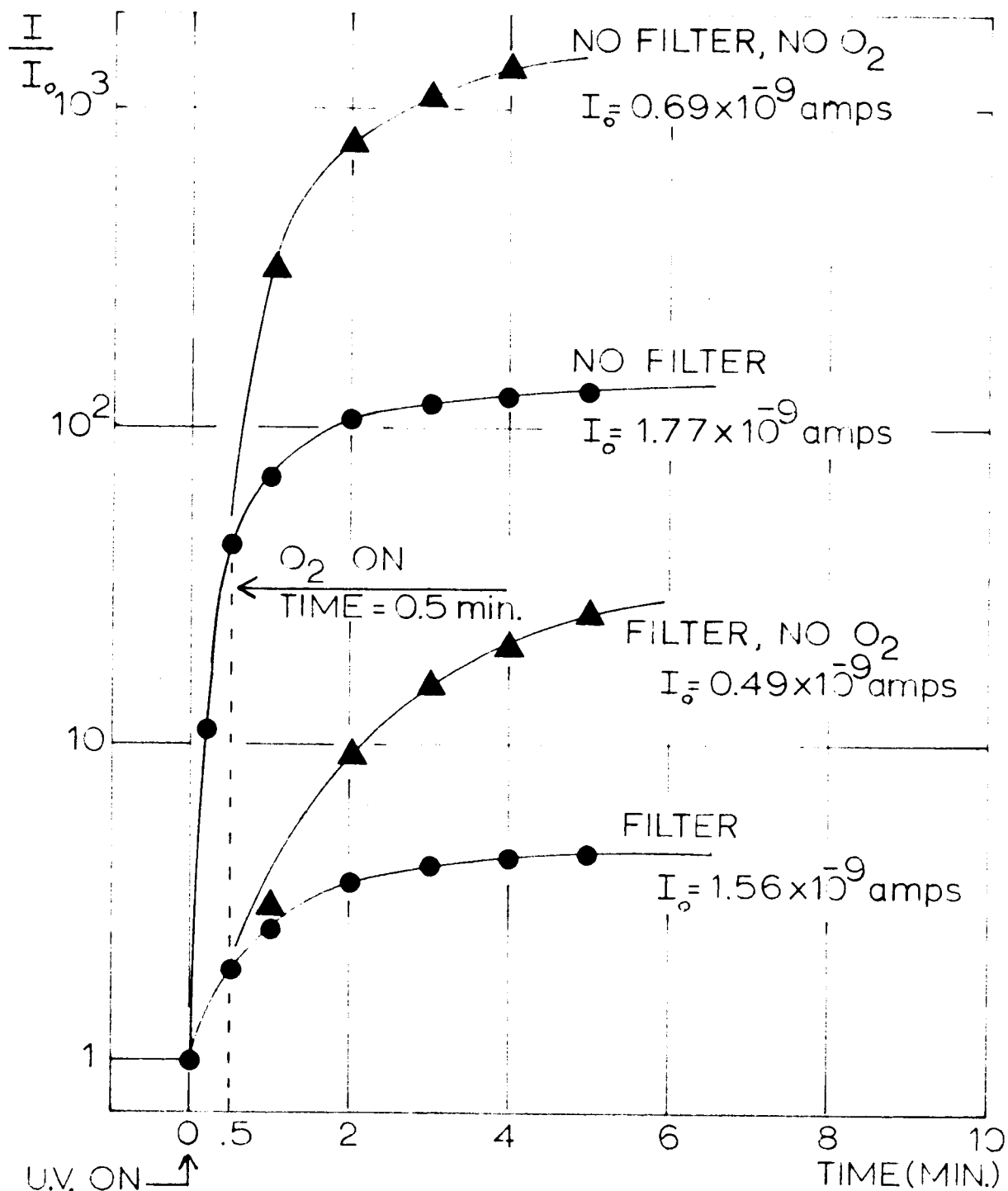
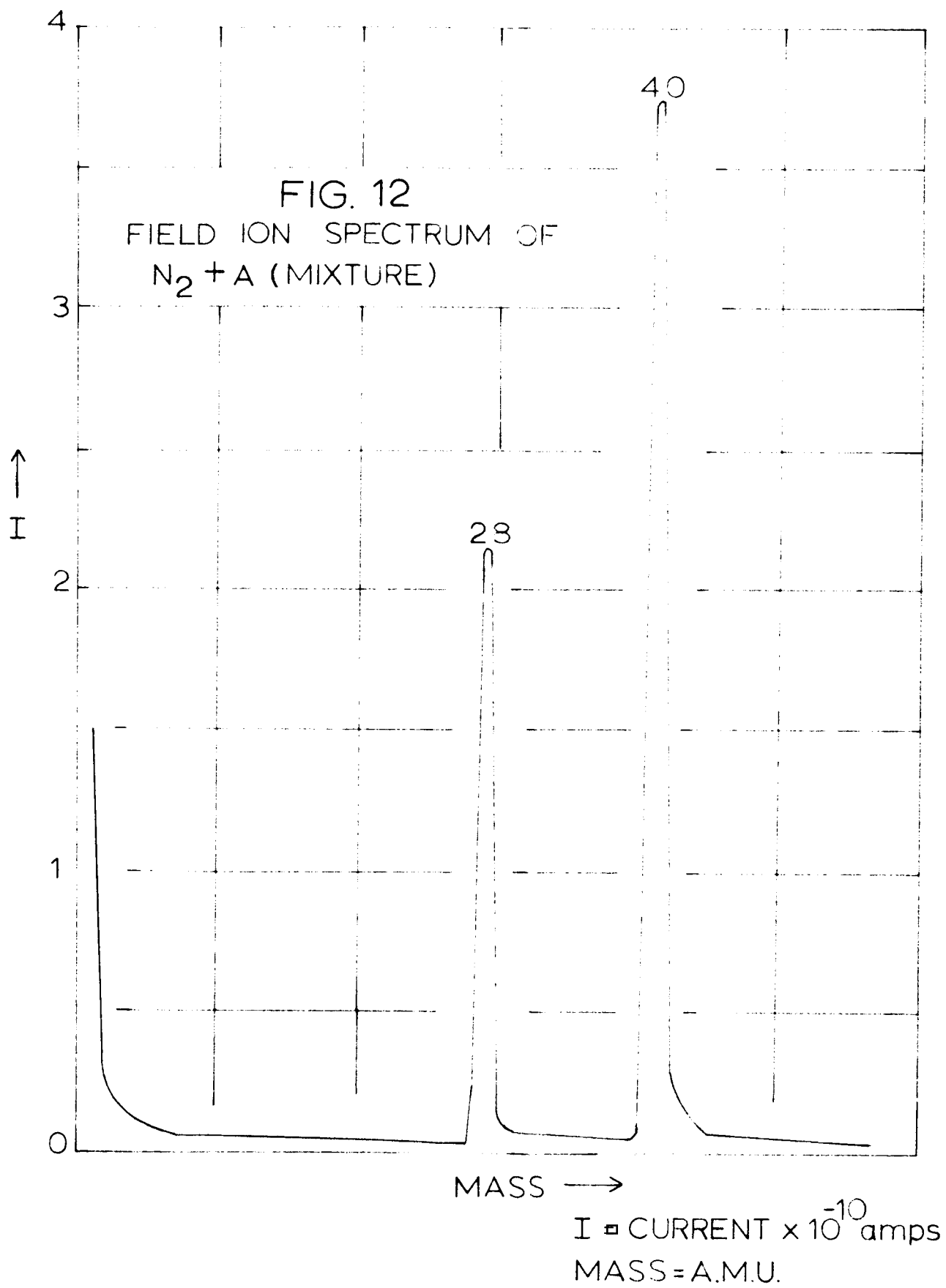


FIG. 11

ZnO CURRENT vs TIME



CONTAMINATION OF MOS FIELD EFFECT TRANSISTORS BY ALKALI IONS EMITTED FROM
HOT TUNGSTEN OR MOLYBDENUM FILAMENTS - REMOVAL BY ELECTRIC FIELDS

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Introduction

The generation of positive ion currents by heated metals was reported many years ago⁽¹⁾. The ions have been shown⁽²⁾ to be due in some cases to residual Na and K in the metal. The magnitude of the ion current in certain cases is known to depend upon the presence of specific ambient gases⁽³⁾.

It has been suggested⁽⁴⁾ that this alkali ion current is responsible for some, if not all, of the alkali contamination observed in MOS Field Effect Transistors. (Hot tungsten or molybdenum wires are used to evaporate the aluminum to form the gate.)

Experiments

To observe the ion current the simple apparatus of Fig. 1 was set up. The field plates shown in Fig. 1 were used to investigate the deflection of ions emitted by the hot filament⁽⁵⁾.

In the first experiment, the field plates were unbiased, the tungsten was heated to 1190°C (optical pyrometer, corrected for emissivity) and the positive ion current to the collector was observed for some twenty hours. The current decreased monotonically but at the end of twenty hours significant currents (i.e., $1.3 \cdot 10^{-8}$ amps/cm²) were still observed. A typical

current-time plot is shown in Fig. 2, tests at other temperatures indicated that the ion current is controlled by the diffusion of the alkali ions in the filament. Experiments were run with other tungsten and molybdenum filaments; in all respects their behavior was similar to that in Fig. 2.

In the next experiment the field plates shown in Fig. 1 were biased and the decrease in collector current observed. For a 250 volt field plate bias (corresponding to a linear field of 66 volts/cm) the ion current fell immediately to some 10^{-12} amps and then rose slowly to $3 \cdot 10^{-9}$ amps/cm² and then remained essentially constant with time. This is shown in Fig. 2 where the data has been corrected to be comparable with the earlier experiments.

At all field plate voltages this typical saturation effect was observed. When the voltage was applied the ion current fell to the noise level, then rose slowly to some value below that observed at zero field. The effect was small at 250 volts but it can be seen in Fig. 2. We suggest that at zero field the ion current is partially controlled by a cloud of positive ions around the filament. If a bias is applied to the field plates, some of the ions are drawn off, lowering the collected ion current. The diffusion of ions to the surface of the filament then begins to increase and the collected ion current increases concurrently. One might consider this as a typical saturation current problem somewhat like those observed in hot cathode vacuum tubes.

Conclusions

The positive ion current from a hot filament may be reduced by heating the filament for a long time to remove the impurities or by simply applying a transverse electric field to keep the ions from the substrate.

The field does not affect the flow of neutral aluminum atoms. (Al has an ionization potential of 5.9 ev and is not ionized on hot metals to any appreciable degree.)

System Design

Scaling up the system of Fig. 1 should present no problems, the highest energy ions will have no more than a few ev of energy if the filament is D.C. ground. However, the designer should be aware that hot filaments are copious emitters of electrons and that any insulating or ungrounded substrate will therefore acquire a negative charge. This may in turn increase the flow of positive ions to the substrate. An Electron-Ion-Substrate effect of this type may explain some of the variations in alkali contamination observed in device production.

This study was part of a long term program on the surface phenomena of metals and semiconductors in various environments.

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4. Private communication, Dr. Lowell Clark
Motorola Semiconductor Products, Phoenix, Arizona
5. Mr. James Payne constructed the apparatus and ran most of the experiments. His help is gratefully acknowledged.

57

10⁻⁸

10⁻⁹

10⁻¹⁰

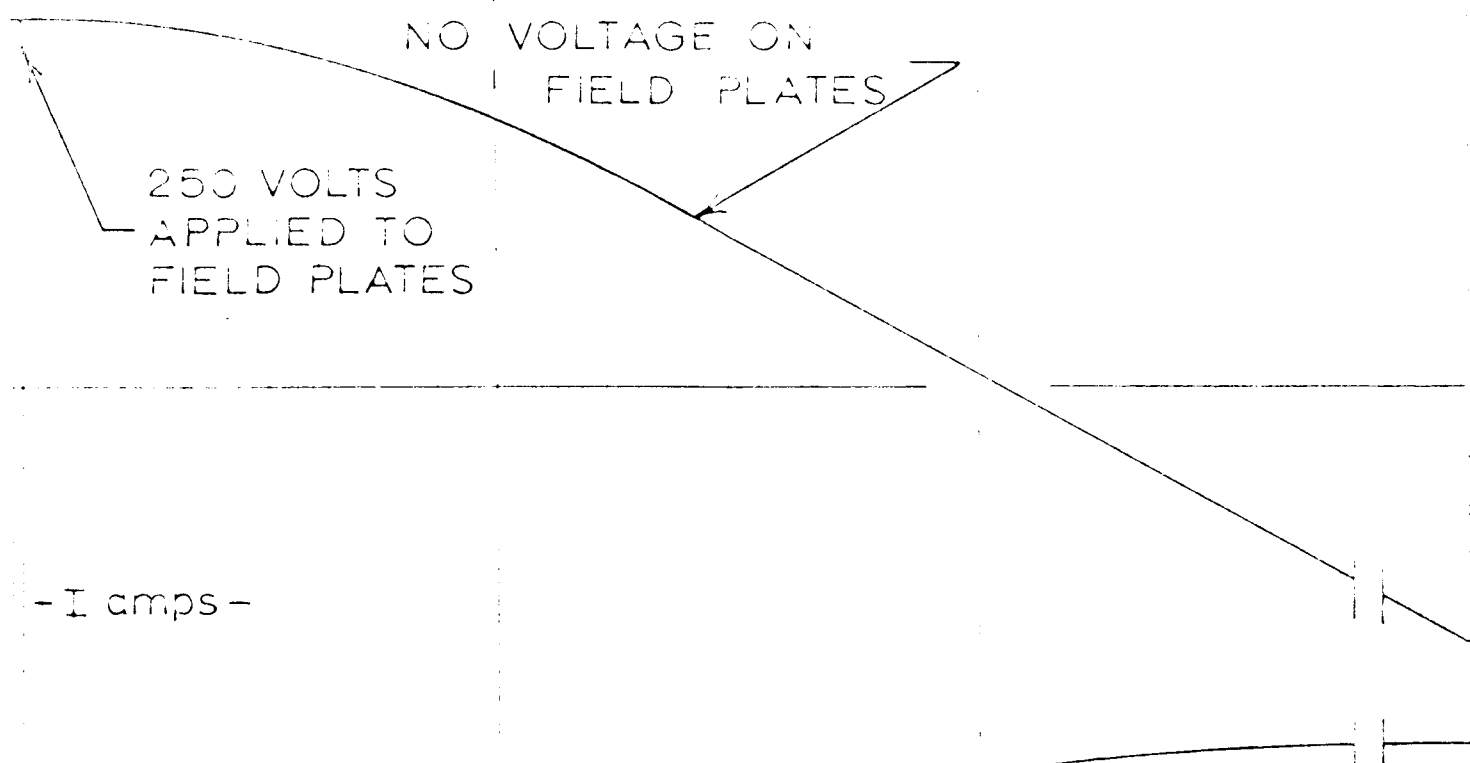


FIG. 2

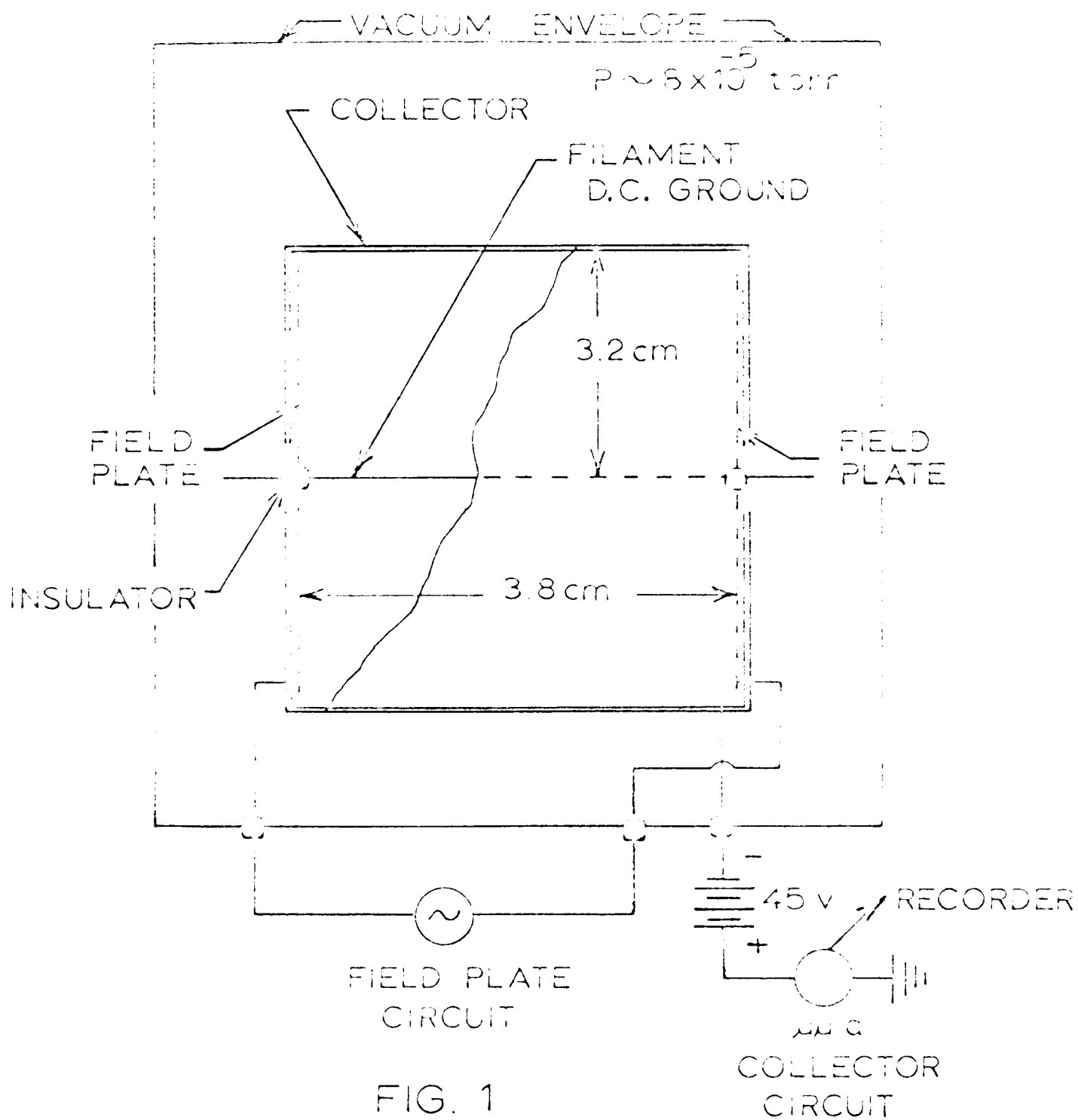
POSITIVE ION CURRENT vs TIME

tungsten filament 0.051cm D X 3.5cm in length

$T=1190^{\circ}\text{C}$ corrected

1 10 100 1000
↑ 1 hr. ↑ 10 hrs.

TIME - MIN
from turn-on of filament
heater current



EXPERIMENTAL SET UP

(scale - none)